

FLUID LOSS REDUCER FOR HIGH TEMPERATURE HIGH PRESSURE WATER  
BASED-MUD APPLICATION

Background of the Invention

5       Drilling fluids, commonly referred to as drilling  
muds, are complex mixtures of chemicals. They are required  
to cool and lubricate the drill bit, suspend formation  
cuttings, lift them to the surface, and control formation  
pressure during the drilling of oil wells.

10       For the most part, the liquid bases are aqueous  
solutions, oils or emulsions of aqueous and oily materials,  
to which viscosifiers, dispersants, emulsifiers, weighting  
agents, fluid loss agents, pH control agents, salts,  
lubricants, select polymers, corrosion inhibitors,  
15 biocides, are usually added to enable the muds to meet the  
needs for particular drilling operations.

Drilling muds are usually classified as either water-  
based muds (WBM) or oil-based muds (OBM), depending upon  
the character of the continuous phase of the mud, although  
20 water-based muds may contain oil and oil-based muds may  
contain water.

Oil-based muds generally use hydrocarbon oil as the  
main liquid component with other materials such as clays or  
colloidal asphalts added to provide the desired viscosity  
25 together with emulsifiers, polymers and other additives  
including weighting agents. Water may also be present, but  
in an amount not usually greater than 50 volume percent of  
the entire composition. If more than about 5% volume water  
is present, the mud is often referred to as an invert  
30 emulsion, i.e., water-in-oil emulsion.

Water based muds conventionally comprise viscosifiers,  
fluid loss control agents, weighting agents and other  
additives including lubricants, emulsifiers, corrosion

inhibitors, salts and pH control agents. The water makes up the continuous phase of the mud and is usually present in any amount of at least 50 volume percent of the entire composition. Oil is also usually present in minor amounts  
5 but will typically not exceed the amount of the water so that the mud will retain its character as a water continuous phase material.

Potassium-muds are the most widely accepted water mud system for drilling water-sensitive shales.  $K^+$  ions attach  
10 to clay surfaces and lend stability to shale exposed to drilling fluids by the bit. The ions also help hold the cuttings together, minimising dispersion into finer particles. Potassium chloride (KCl) is the most widely used potassium source. Others are potassium acetate, potassium  
15 carbonate, potassium lignite, potassium hydroxide and potassium salt of partial hydrolyzed polyacrylamide (PHPA). For rheology control, different types of polymers are used, for example XC polymer (Xanthan gum) and PHPA. For fluid-loss control, mixtures of starch and polyanionic cellulose  
20 are often used. Carboxymethyl starch (CM starch), hydroxy propyl starch (HP starch), carboxymethylcellulose and sodium polyacrylate (SPA) are also used. PHPA is widely used for shale encapsulation.

Salt-water muds contain varying amounts of dissolved  
25 sodium chloride (NaCl) as a major component. Undissolved salt may also be present in saturated salt muds to increase density or to act as a bridging agent over permeable zones. Starch and starch derivatives for fluid-loss control and Xanthan gums for hole-cleaning are among the few highly  
30 effective additives for salt-water muds.

Sea-water mud is a water based mud designed for offshore drilling whose make-up water is taken from the

ocean. Sea-water has relatively low salinity, containing about 3 to 4% by weight of NaCl, but has a high hardness because of  $Mg^{+2}$  and  $Ca^{+2}$  ions. Hardness is removed from sea water by adding NaOH, which precipitates  $Mg^{+2}$  as  $Mg(OH)_2$  and  
5 by adding  $Na_2CO_3$ , which removes  $Ca^{+2}$  as  $CaCO_3$ . Mud additives are the same as those used in freshwater muds: bentonite clay, lignosulfonate, lignite, carboxymethylcellulose or polyanionic cellulose and caustic soda. XC polymer may also be used in place of bentonite.

10 Silicate-mud is a type of shale-inhibitive water mud that contains sodium or potassium silicate as the inhibitive component. High pH is a necessary characteristic of silicate muds to control the amount and type of polysilicates that are formed. Mud pH is  
15 controlled by addition of NaOH (or KOH) and the appropriate silicate solution. Silicate anions and colloidal silica gel combine to stabilize the wellbore by sealing microfractures, forming a silica layer on shales and possibly acting as an osmotic membrane, which can produce  
20 in-gauge holes through troublesome shale sections that otherwise might require an oil mud.

Lime-mud is a type of water based mud that is saturated with lime,  $Ca(OH)_2$ , and has excess, undissolved lime solids maintained in reserve. Fluid-loss additives  
25 include starch, HP-starch, carboxymethylcellulose (CMC) or polyanionic cellulose (PAC).

Apart from cooling and lubrication of the drilling bit, evacuation of the cuttings to the surface and control of the formation pressure, drillings muds must ensure to  
30 minimize invasion into permeable zones.

The drilling fluid creates a filter cake that imparts low permeability to the face of the permeable formation.

The ideal filter cake comprises a relatively thin and hard layer as opposed to thick viscous coating. Pressure in the bore hole exceeds the pressure in the permeable formation and thereby creates the filter cake which further results  
5 in liquid from the drilling fluid moving into the permeable formation. This leaves a layer of the filter cake on the face of the hole. Liquid permeating this filter cake and the formation is called filtrate. As the thickness of the filter cake increases, the volume of fluid loss also  
10 increases. The thinner the filter cake, the lower the fluid loss. A thick wall cake will lead not only to high fluid loss, but also to a reduction in the diameter of the well bore.

The function of the fluid loss control agents is to  
15 delay, prevent or at least limit as far as possible fluid losses that may be sustained by the drilling fluids during the drilling operation. However, most of fluid loss control agents used in water based muds such as polyanionic cellulose, carboxymethylcellulose, starch, etc. give also  
20 rheology to the mud. This is therefore limiting the level of fluid loss control agent that can be used. In this context, an additive that would only control the fluid loss properties would allow more flexibility in term of level usage. This can become really critical when severe  
25 drilling conditions require an ultra-low permeability barrier between the well bore and the formation.

Additionally, the compounds added to the mud must withstand the high temperature/high pressure (HTHP) in the wells. Materials that are described in the art as HTHP  
30 fluid loss control aids have actually a poor stability under these extreme conditions of temperature and pressure.

For high salinity and high temperature conditions,

acrylamido-methyl-propane sulfonate polymers (AMPS polymers) have been developed. However, these polymers are showing limited performance above 120°C.

5    Summary of the Invention

          The present invention relates to an improved fluid loss reducer for use in water-based drilling mud. It is a principal object of the present invention to provide an improved fluid loss reducer that can be used at high levels  
10    and under conditions of high temperature and high pressure in water-based muds.

          This invention is based upon the unexpected discovery that an oil soluble polymer in a form of a gel can be used as fluid loss additive for drilling water-based mud  
15    compositions. By utilizing such an oil soluble polymer in drilling water-based muds, greatly improved high temperature stability and improved shear resistance can be obtained.

          The present invention more specifically discloses a  
20    water-based drilling mud comprising an aqueous phase wherein the aqueous phase contains an oil soluble polymer in a form of a gel as fluid loss reducer.

          The water-based mud drilling fluid according to the instant invention comprises water or salt water,  
25    viscosifiers, fluid loss control agents, weighting agents and an oily phase, and other conventional additives selected from the group consisting of emulsifiers, lubricants, corrosion inhibitors, salts and pH control agents.

30          The present invention more specifically discloses a water-based drilling fluid mud comprising:

- (1) from 50 to 90% of the aqueous phase,
- (2) from 0.01 to 0.5% of pH controllers,

- (3) from 0.1 to 5% of viscosifiers,
- (4) from 0.01 to 30% of salts,
- (5) from 0.1 to 3% of emulsifiers,
- (6) from 4 to 60% of weighting agents,
- 5 (7) from 0 to 15% of clays, and
- (8) from 0.1 to 20% of oil soluble polymer in form of a gel as fluid loss reducer, said percentages being based on the weight of the mud.

The subject invention further reveals a process for  
10 preparing an oil soluble polymer fluid loss control agent comprising the steps of dissolving at least one polymer in a hydrocarbon oil to form a clear solution or a gel, adding an emulsifier to the solution or the gel, and keeping the mixture under conditions of agitation until a clear creamy  
15 mixture is obtained.

The present invention also discloses a method of lubricating a drilling bit during the drilling of a well which comprises circulating a water-based drilling mud in the vicinity of the drilling bit wherein the water-based  
20 drilling mud is comprised of an aqueous phase wherein the aqueous phase contains an oil soluble polymer in the form of a gel as a fluid loss reducer.

#### Detailed Description of the Invention

25 The water-based drilling fluid mud of the present invention is comprised of an aqueous phase, wherein the aqueous phase contains an oil soluble polymer in the form of a gel as a fluid loss reducer. The water-based drilling fluid mud will typically be comprised of the aqueous phase,  
30 a pH controller, a viscosifier, a salt, an emulsifier, a weighting agent, clay, and an oil soluble polymer in the form of a gel as a fluid loss reducer. This mud composition will normally contain 50% to 90% of the aqueous

phase, 0.01% to 0.5% pH controllers, 0.1% to 5%  
viscosifiers, 0.01% to 30% salts, 0.1% to 3% emulsifiers,  
4% to 60% weighting agents, 0% to 15% clays, and 0.1% to  
20% of oil soluble polymers in the form of a gel as a fluid  
5 loss reducer; based upon the weight of the mud.

The water-based drilling fluid mud will more typically  
contain 55% to 70% of the aqueous phase, 0.1% to 0.3% pH  
controllers, 0.4% to 2% viscosifiers, 5% to 15% salts, 0.5%  
to 2% emulsifiers, 10% to 25% weighting agents, 5% to 10%  
10 clays, and 0.5% to 2.5% of oil soluble polymers in the form  
of a gel as a fluid loss reducer; based upon the weight of  
the mud.

The oil soluble polymer is highly efficient in small  
proportions as a fluid loss reducer. It may be  
15 incorporated in an amount of 0.1 to 10%, most preferably in  
an amount of 0.5 to 2.5% based on the weight of the mud.

The suitable polymers for preparing the emulsion used  
according to the invention are organo-soluble polymers and  
may be selected from the group constituted by the linear  
20 polymers, the grafted polymers, the branched polymers and  
the cross-linked polymers.

A wide variety of polymers or copolymers can be  
utilized in this invention. These polymers may be prepared  
by polymerization using bulk, emulsion, suspension,  
25 solution (anionic, cationic, radical, controlled radical),  
and condensation polymerization technique. Batch, semi-  
continuous or continuous polymerization processes are  
suitable for utilization in the synthesis of the polymer.

The monomers that can be employed are typically  
30 selected from the group consisting of styrene, substituted  
styrene, alkyl acrylate, substituted alkyl acrylate, alkyl  
methacrylate, substituted alkyl methacrylate,  
acrylonitrile, methacrylonitrile, acrylamide,

methacrylamide, N-alkylacrylamide, N-alkylmethacrylamide, isoprene, butadiene, ethylene, vinyl acetate, vinyl ester of versatic acids containing from 9 to 19 carbon atoms (C<sub>9</sub> to C<sub>19</sub>), and combinations thereof. Functionalized versions  
5 of these monomers may also be used. Some representative examples of the selective monomers, which can be used, include styrene, alpha-methylstyrene, para-methylstyrene, para-tertbutylstyrene, vinyltoluene, (M)ethyl(Me)acrylate, 2-ethylhexyl(Me)-acrylate, butyl(Me)acrylate,  
10 cyclohexyl(Me)acrylate, isobornyl(Me)acrylate, isobutyl(Me)acrylate, p-terbutyl-cyclohexyl(Me)acrylate, butadiene, isoprene, ethylene, veova, vinyl acetate, acid(Me)acrylic, hydroxy-ethyl(Me)acrylate, glycidyl methacrylate, sodium benzenesulfonate and combinations  
15 thereof.

The typical but non-limiting examples of suitable polymers, that are useful in this invention, are commercially available from a wide variety of sources. For instance, Eliokem sells styrene-acrylate or styrene-  
20 butadiene copolymers under the trade name Pliolite<sup>®</sup>, such as Pliolite<sup>®</sup> DF01, Pliolite<sup>®</sup> DF02, Pliolite<sup>®</sup> DF03, Pliolite<sup>®</sup> VTAC-H, Pliolite<sup>®</sup> VT and Pliolite Ultra 200<sup>®</sup>, substituted styrene-acrylate copolymers under the trade name Plioway<sup>®</sup>; Rohm sells acrylate resins under the trade name Plex<sup>®</sup>,  
25 Goodyear Chemicals sells styrene-butadiene rubber under the trade name Plioflex<sup>®</sup>; Kraton S.A. sells block copolymers styrene-butadiene and their hydrogenated version under the trade name Kraton<sup>®</sup>.

A wide variety of crosslinking agents can be utilized  
30 in carrying out the polymerization to produce these polymers. Some representative examples of crosslinking agents which can be utilized include difunctional acrylates, difunctional methacrylates, trifunctional



acrylates, trifunctional methacrylates, allyl maleate and divinylbenzene.

Various other components are added to provide the desired properties for the drilling mud. Various polymers  
5 are used to control the mud rheology and therefore to keep the rock cuttings in suspension as they move up to the borehole to the surface. An alkaline substance, such as caustic soda, provides alkalinity to the system. Weighting agent, such as barite, is also used.

10 The water-mud may be a potassium mud, a salt water mud, a sea water mud, or a lime mud.

The present invention further reveals a process for preparing the oil soluble polymer fluid loss control agent.

The oil soluble polymer fluid loss control agent may be  
15 prepared by dissolving polymers in a hydrocarbon oil to form a clear solution or a gel, adding an emulsifier and keeping the mixture under stirring until a clear creamy mixture is obtained; optionally an emulsion can be prepared by adding water under high shear stirring.

20 The oil soluble polymer thus obtained is added to a water-based mud prepared by conventional methods, either in replacement of the conventional fluid loss reducers, or in addition to said conventional fluid loss reducers.

The organic liquids, which may be utilized in the  
25 instant invention, are selected with relation to the polymer solubility. The hydrocarbon oil is selected from the group comprising of aromatic hydrocarbon, chlorinated aliphatic hydrocarbons, aliphatic hydrocarbons, cyclic aliphatic ethers, aliphatic ethers, or organic aliphatic  
30 esters and mixture thereof. Preferably hydrocarbon oils are selected from the groups of synthetic hydrocarbons and organic aliphatic ester, most preferably from the group of

well fluids (base oil) useful in the rotary drilling process. The properties of the base oil can vary however, so that it is usually necessary to perform solubility test to determine the appropriate amount of oil to prepare the  
5 emulsion.

The level of emulsifier added to the polymer solution is typically 1 to 30%, preferably from 3 to 20%, most preferably from 5 to 15% based on the weight of the polymer solution/emulsifier mixture. The preferred emulsifiers for  
10 use in the instant invention include ionic and non ionic derivatives and mixtures thereof. Specific examples of preferred emulsifiers that are useful in the instant invention include alkyl sulfate, alkyl benzene sulfonate, alkyl ethersulfates, sulfonated oleic acid, alkylphenol  
15 ethersulfates, sulfosuccinates, phosphoric ester, fatty acid amides, fatty acid amines, fatty alcohol polyglycolethers, modified fatty alcohol polyglycolethers, alkyl polyglycosides, modified alkyl polyglycosides, alkylphenol polyglycolethers, fatty acid polyglycolethers,  
20 sorbitan fatty acid esters. More preferably, the emulsifier is chosen in the group comprising alkyl ethersulfates and fatty acid amides and their derivatives.

Optionally, water can be added to the polymer solution/emulsifier mixture. The level of water is  
25 typically 0 to 60%, preferably from 10 to 50%, most preferably from 20 to 40% based on the weight of the polymer emulsion.

The level of polymers in the polymer solution is typically about 1 to about 40%, preferably from 5 to 35%,  
30 most preferably from 15 to 25% based on the weight of the polymer solution. It is important for the polymer backbones to be soluble in the organic liquid.

The present invention further reveals the use of an oil soluble polymer in a form of a gel as a fluid loss reducer in a water-based mud.

5 The instant invention further reveals a method of lubricating a drill pipe when drilling well, said method comprising circulating a water-based drilling fluid containing an oil soluble polymer in a form of a gel as a fluid loss reducer.

10 The oil soluble polymers in a form of a gel, according to the instant invention, allow a good thermal stability and avoid any rheological contribution. They may be used at high temperature and high pressure conditions. Moreover, they improve the quality of the filter cake and also improve the water-based muds lubricity performance.

15 This invention is illustrated by the following examples that are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and  
20 percentages are given by weight.

Example 1 (Preparation of the oil emulsion and of the polymer in a form of a gel)

The preparation of an oil emulsion is as follows:

25 First, 100 grams of base oil (Ex: Radiagreen®) is mixed with 33.3 grams of emulsifier (Disponil FES®) and kept under stirring for 5 minutes. Then, 36.7 grams of water are slowly incorporated to the oil/ emulsifier mixture which is stirred under high shear for 20 minutes.

30 If needed, defoamer is added to the preparation. The particle size of the resulting emulsion is then measured.

The polymers in a form of a gel are prepared using the

same recipe: 100 grams of base oil is replaced by 100 grams of 80/20 polymer gel which is prepared by the dissolution of 20 grams of polymers in 80 grams of base oil.

5       The polymers used were either linear, grafted, branched or cross-linked.

Example 2 (Preparation of the water-based muds)

10       The base muds were prepared by utilizing a conventional laboratory method. The muds were then placed in aging cells, pressurized at  $6.9 \times 10^5$  Pa (100 psi), and heated for 4 hours at 95°C (203°F) and/or 16 hours at 95°C (203°F) and/or 16 hours at 130°C (266°F). The aging cells were cooled down to room temperature, depressurized and then the rheology of the mud was measured on a Fann Model  
15       35 viscometer at 50°C (122°F). Static filtration measurement was performed with standard API filtration cell at  $6.9 \times 10^5$  Pa (100 psi) and 25°C (77°F).

20       In order to test the emulsion property at high pressure and high temperature, static filtration measurements at  $34.5 \times 10^5$  Pa (500 psi) and 95°C (203°F) were performed. The results, obtained with the water-based mud containing the polymeric emulsion, are directly compared with the water-based mud (control) and the water-based mud containing the oil emulsion.

25       The different mud formulations used are shown in table I.

TABLE I

INGREDIENTS	Formulation 1 (water-based mud) (g)	Formulation 2 (g)	Formulation 3 (g)
Freshwater	276.5	265.2	265.2
KCl	45	45	45
Caustic Soda	0.3	0.3	0.3
Soda Ash	0.3	0.3	0.3
Polyanionic Cellulose 1	0.75	0.75	-
Polyanionic Cellulose 2	3.0	3.0	-
Xanthan gum	0.75	0.75	1.25
OCMA clay	35	35	35
Barite	58.31	58.31	58.31
Emulsion	-	31.9	31.9

Formulation 1 (base-mud) is reference based mud  
5 comprising ionic cellulose as fluid loss reducer.

Formulation 2 is a water-based mud with the same  
composition as formulation 1, but also containing an oil  
soluble polymer according to the instant invention as fluid  
loss reducer ("on top" formulation). For the preparation  
10 of formulation 2a, the emulsion does not contain any  
polymer. For the preparation of formulation 2b, a linear  
polymer is used. For the preparation of formulation 2c, a  
cross-linked polymer is used.

In formulation 3, polyanionic cellulose is replaced by  
15 the oil soluble polymer according to the instant invention.  
A cross-linked polymer is used.

The results obtained with the non cross-linked and the  
cross-linked polymers emulsion over the temperature range  
of 25°C -95°C (77°C -200°F) are directly compared with the  
20 water-based mud (control).

As shown in table II, the polymeric emulsion gives  
significative better results in term of static filtration  
than the reference formulation without having any impact on  
mud rheology.

TABLE II

Muds formulations		Rheology Fann 35 SA viscometer										Filtration Fann HTHP filter press	
		600 rpm	300 rpm	200 rpm	200 rpm	100 rpm	100 rpm	100 rpm	100 rpm	Plastic viscosity (cps = 10 <sup>-4</sup> Pa.s)	yield point (lb/100 ft <sup>2</sup> = 0.479 Pa)	Room t°C ml	95°C ml
Formulation 1		78	52	43	31	9	7				26	4.0	13.6
		76	51	43	30	8	6				26	4.8	14.0
Formulation 2a: Oil emulsion (on top)		79	54	42	28	7	5			25	29	2.0	10.0
		73	48	37	25	6	4			25	23	1.6	8.0
Formulation 2b: Linear polymer (on top)		73	53	45	33	13	11			20	33	2.4	8.8
		78	56	46	33	8	6			22	34	-	8.4
		86	60	49	34	8	6			26	34	2.0	8.4
		75	51	40	28	7	5			24	27	1.6	6.4
Formulation 2c: Cross-linked polymer (on top)		86	59	48	32	7	6			27	32	1.6	6.4
		90	62	50	34	8	6			28	34	-	5.6
		89	61	48	33	7	5			28	33	-	6.0
		88	59	47	32	7	5			29	30	1.6	5.6
		88	60	49	33	8	6			28	32	1.6	6.0
Formulation 3: Cross-linked polymer (replacement)		33	18	14	11	4	3			5	3	4.8	-

<sup>1</sup> Are substituted styrene acrylate copolymers.

Filtration value in ml is significantly reduced when polymer such as VTACH<sup>®</sup>, U200, XPR036, Pliolite VT<sup>®</sup>, or Kraton G<sup>®</sup> was added in re-emulsified form in the standard  
5 water-based drilling fluid formulation. This value is further reduced when the above polymer is replaced by a cross-linked polymer such as Pliolite DF01, DF02, DF03, CPR7676, CPR7755. Replacement in water-based mud of fluid  
10 loss reducers by the polymer emulsion leads to equivalent level of filtration versus water-based mud.

As it can be seen in Table III, filtration value in ml is significantly reduced after high temperature aging when cross-linked polymer such as Pliolite DF01<sup>®</sup> was used with an emulsifier package (Disponil FES<sup>®</sup>/ Kleemul<sup>®</sup>) in the standard  
15 water-based drilling fluid formulation.

TABLE III

Muds Formulations		Rheology Fann 35 SA viscometer								Filtration Fann HTHP filter press
								Yield point (lb/100 ft <sup>2</sup> = 0.479 Pa)	Room t°C	
		600 rpm	300 rpm	200 rpm	200 rpm	6 rpm	3 rpm	Plastic viscosity (cps)	95°C  ml	
Formulation 1	Pliolite DF01 <sup>®</sup>	After aging 16 hours at 95°C (200°F)								5.2
		38	26	20	14	4	3	12	14	
		64	45	36	25	7	5	19	26	
		After aging 16 hours at 130°C (266°F)								
Formulation 1		29	20	16	11	3	2	9	11	20.4
Formulation 3c	Pliolite DF01 <sup>®</sup>	40	27	21	15	4	3	13	14	6.8



While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art  
5 that various changes and modifications can be made therein without departing from the scope of the subject invention.